

High temperature separation membranes for hydrogen purification and carbon capture

K.A. Berchtold (MST-7)¹, J.S. Young (X-2)², K.W. Dudeck (MST-7)¹

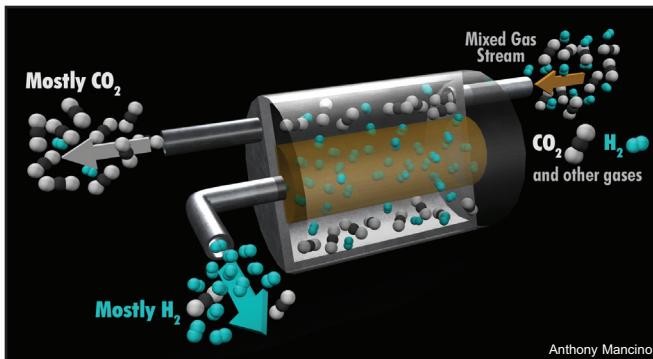
While alternative and renewable energy sources will gradually increase their contributions to the world's energy supply, most energy projections agree that conventional fossil energy generation will continue to dominate for the foreseeable future. U.S. energy demand alone currently results in billions of tons of annual carbon dioxide emissions. These greenhouse gas emissions create a variety of environmental challenges and correspondingly, drive national and international research and development initiatives focused on carbon sequestration.

Capturing carbon dioxide from mixed-gas streams is the critical first step upon which all carbon sequestration methods depend. A new and economical technology for the separation and capture of carbon dioxide from fossil fuel conversion processes could lead to a significant reduction in greenhouse gas emissions to the atmosphere. To be technically and economically viable, a successful separation method must be applicable to industrially relevant gas streams at realistic temperatures and able to handle the associated large gas volumes.

Limits of current technology

Current CO₂ separation technology does not address the entire range of separation applications as economically as will be required for the large scale sequestration of CO₂. For example, amine-based technologies work only at low temperatures and pressure-swing absorption and cryogenic distillation have significant energy penalties (up to 35%) for separating CO₂. In contrast, polymer-based membrane separations are less energy intensive, requiring no phase change in the process, and typically provide low-maintenance operations. Polymer membranes have been used successfully in a number of industrial applications, including the production of high-purity nitrogen, gas dehydration, removal of acid gases, and recovery of hydrogen from process streams for recycle.

However, successful use of a polymer membrane in a synthesis gas separation requires a membrane that is thermally, chemically, and mechanically stable at high temperature and high pressure. Unfortunately, the com-



Anthony Mancino

This simplified model of the single tube membrane module shows a mixed gas stream (composed of hydrogen, CO₂, and other gases) entering the outer tube. The membrane blocks most of the CO₂ but allows hydrogen to pass through to the inner chamber where it can be collected and used as fuel. The separated carbon-rich stream exits the outer tube at high pressure, ready for transport to a carbon storage repository.

mercially available polymeric materials currently employed are not stable in such demanding environments to the degree required. Consequently, there is a compelling need for membrane materials that can operate under demanding environmental conditions for extended periods of time while providing a level of performance that is economically sustainable by the end user.

Alternatives to polymeric membranes are the inorganic membranes, which include zeolites,

carbon molecular sieves and selective surface-flow membranes. These inorganic membranes currently suffer from lack of reproducibility, densification due to humidity and elevated temperatures, and high-cost fabrication. Given these limitations, mixed-matrix membranes and crosslinked membranes have been suggested as future viable development pathways. Mixed-matrix membranes are composed of carbon molecular sieves or zeolites embedded in a polymer matrix. Although permeabilities and selectivities have been increased above the traditional Robeson upper boundary for polymers, application temperatures remain limited by the polymer matrix. Alternatively, crosslinked membranes can reduce the plasticization effects at elevated pressures as well as increase membrane selectivity; however, permeability is typically adversely affected. Hence, the development of high performance polymer membranes remains an attractive and viable engineering approach to filling the critical need for high temperature membrane separations.

Collaboration aims for new development

In collaboration with Pall Corporation, University

¹Polymers and Coatings Group, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

²Thermonuclear Applications Group, Applied Physics Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Materials Science and Technology Division Research Highlight

of Colorado, and Idaho National Laboratory, Los Alamos National Laboratory scientists are leading an effort aimed at developing high-temperature polymeric-metallic composite membranes to address the aforementioned limitations of the current state of the art and the corresponding separations needs of the utility sector. The work focuses on a pre-combustion capture approach integrating the high-temperature polymeric-metallic composite membranes into an advanced integrated gasification combined-cycle (IGCC) process.

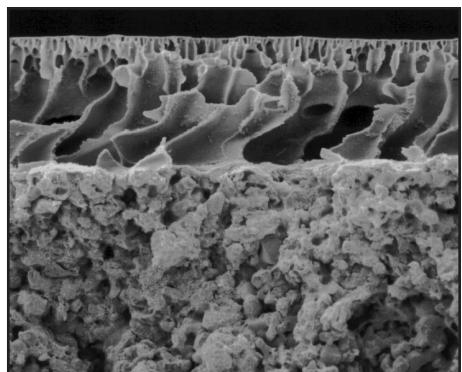
The primary goals of the project are to develop advanced polymeric materials and unique polymeric-metallic composite membrane structures achieving the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability at elevated temperatures ($>150^{\circ}\text{C}$). Stability requirements focus on tolerance to the primary synthesis gas components and impurities at various locations in the process. Because temperature and pressure conditions and the composition of the gas stream vary throughout IGCC power production, the project has focused on modeling and evaluating membrane performance at several different points along the process to achieve optimal results.

The collaborative research effort is focused on both the continued development of an existing generation of composite membranes as well as the rational design and development of new high temperature materials with enhanced gas separation properties (primarily H_2/CO_2 selectivity and H_2 flux) and substantial chemical, mechanical, and thermal stability. The team is also developing a unique methodology to understand, predict, and optimize the long-term behavior of the material under challenging operating conditions. The most promising composites developed to-date by the team utilize a polybenzimidazole (PBI)-based selective layer supported by unique porous metal substrate (Pall AccuSep®) with a tailored zirconia intermediate layer serving as the interface between the polymer and the metal support.

Evaluations of these composites at the LANL High Temperature Membrane Development Facility included performance testing in dry gas environments containing H_2 , CO_2 , CH_4 , N_2 , CO , and H_2S from 25 to 400°C on both planar and tubular membrane configurations. Thermal stability and sulfur tolerance were explored via long-term (300+ days) membrane module testing at 250°C . Additionally, out-of-the-laboratory slip-stream testing was conducted on a natural gas fuel processor in early FY06. The test stream consisted of the fully hydrated natural gas reformat exiting the water gas shift reactor. Testing was conducted from 250 – 400°C . The membrane performance under hydrated conditions was actually improved over the ideal laboratory conditions.

Project progress to date indicates that the PBI-based composite membranes under development can function at significantly higher temperatures ($>350^{\circ}\text{C}$) than current commercially

Scanning electron microscopy image of a polybenzimidazole (PBI)-based polymer-metallic composite membrane cross-section. The polymeric selective layer is the thin skin at the surface of the asymmetric PBI film.



available polymeric membranes ($<150^{\circ}\text{C}$). The membranes maintain a commercially attractive selectivity between H_2 and CO_2 even at 400°C . To our knowledge, this is the highest operating temperature reported for a polymer-based membrane. In addition, the PBI-based composite membrane outperforms any polymer-based membrane commercially available or reported in literature for separations involving hydrogen. This achievement is validated via membrane productivity (separation factor and flux) comparisons. Additionally, the improved performance of this technology in an application such as IGCC-integrated capture is further substantiated by the accessible operating temperature range, long-term hydrothermal stability, sulfur tolerance, and overall durability of the composite membrane over a broad range of challenging operating environments relevant to fossil-fuel-based energy production.

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Kathryn A. Berchtold received her Ph.D. in chemical engineering in 2001 from the University of Colorado, Boulder. At Los Alamos National Laboratory she was a Director's funded postdoctoral fellow and is now a technical staff member in MST-7. Research interests include the investigation of the formation, structure, and properties of crosslinked polymeric materials and polymer derived ceramics with an emphasis on development of selective barrier materials for separations applications, photopolymerizations, and reaction engineering.

Jennifer S. Young received her Ph.D. in chemical engineering in 1998 from the University of Colorado where she studied biodegradable photopolymers for orthopedic applications. At Los Alamos National Laboratory, she was a Director's funded postdoctoral fellow and is a technical staff member in the Applied Physics Division.

Kevin W. Dudeck received his B.S. in materials science and engineering from Michigan Technological University in 2001. After working in industry where he gained significant experience in polymer and polymer-derived ceramic development, synthesis, processing, and application, he joined the Laboratory as a technician in 2005.

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